First-principles study of binary austenitic Ni-Cu alloys

Maje Phasha¹, Veronica Morudu¹ and Caroline Mphela¹

¹Advanced Materials Discipline (AMD), MINTEK, South Africa

Abstract. The backbone of the Monel alloys is built on the Ni-Cu system. As a result of their inherent properties such as high strength, toughness and excellent corrosion resistance, these alloys are widely used in marine, chemical and oil industries. A major setback of Ni-Cu alloys in application is the unsatisfactory wear performance. One way to get a grip around this issue is by understanding their fundamental properties. Thus, in order to lay a foundation for future materials development, this study employs first-principles approach to predict structural and mechanical properties of binary Ni-Cu austenitic alloys.

1 Introduction

Nickel (Ni) forms as a base for a wide range of Ni alloys used in numerous engineering applications due to their good mechanical properties and excellent corrosion resistance in various environments [1-3]. This performance is owed to the fact that Ni has the ability to dissolve high concentrations of alloying elements in comparison to other metals and still maintain good metallurgical stability [4]. Mechanical strength can be increased via solid solution [5] or precipitation [6] strengthening mechanism when some of the alloying elements are introduced. One of the attractive features that render Ni-base alloys suitable for use at both cryogenic and high temperatures in the range of 1200°C is that these alloys retain their face-centered-cubic (FCC) crystal structure referred to as austenite phase from solidification to absolute zero temperature. It is for this reason that they are able to maintain high strength, ductility and toughness in this temperature range. One such material is the Monel alloy family, which forms from the Ni-Cu system [4]. In this system, a FCC single phase binary alloys spanning the entire concentration range can be produced as a result of a 100% solid solubility in each other. Due to their combination of high strength and toughness, excellent corrosion resistance, and at times reasonable wear resistance, the Ni-Cu alloys are widely used in the marine, chemical and oil industries for manufacturing components [4, 7]. However, the ever increasing demand from marine industry for improved performance while keeping material cost low has driven efforts to develop new Ni-Cu-based alloys with enhanced mechanical properties, in particular wear resistance. Response to this quest requires a careful material design to improve wear resistance without compromising the excellent corrosion resistance, as well as adoption of advanced manufacturing technologies.

A sound starting point towards designing materials fit for purpose is to create fundamental building blocks on which further developments involving complex compositions are to be
built upon. Despite the simplicity of the Ni-Cu system as shown in Figure 1 [8], most investigations rarely report the mechanical properties of both paramagnetic (PM) and ferromagnetic (FM) binary alloys in the same article. As a result, the current study make use of ab initio calculations to predict structural and mechanical properties of PM and FM binary Ni-Cu alloys. The basis for choosing this computational modelling approach is because it has proven to provide vital insights necessary to understand the inherent properties of materials [9-11]. As such, it is found to be suitable and appropriate to fulfill the objectives of this work.

![Fig. 1. The Cu-Ni phase diagram including the miscibility gap, with dashed lines denoting the magnetic transformation [8].](image)

2 Methodology

First-principles calculations carried out in this work were conducted using densify functional theory (DFT) based CASTEP code embedded in Materials Studio software package [12]. These calculations used a 2x2x2 FCC supercell consisting of 32 atoms with space group #221 (Pm-3m). Robust Vanderbilt ultrasoft pseudopotentials [13] were used to describe the ion-electron interaction within the generalized gradient approximation (GGA) [14] of Perdew-Burke-Ernzerhof (PBE) [15] for PM Ni_{32-x}Cu_x compositions. A plane wave energy cutoff of 500 eV and k-points set of 6x6x6 were sufficient to converge the total energy of the considered systems. Calculations for FM Ni_{32-x}Cu_x compositions were carried out using GGA-PW91 functional with spin polarized [16]. The ground-state structures were optimized using the Brayden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme. The convergence criterion of less than 1x10^{-5} eV/atom, the maximum residual forces of 0.03 eV/Å, maximum residual bulk stress of 0.05 GPa and maximum atomic displacement of 1x10^{-3} Å were utilized.

2.1 Phase stability

The heats of formation calculated using equation 1 below was used to determine the thermodynamic stability of the alloy compositions considered in this study

\[ H_{F}^{Alloy} = \frac{1}{n} E_{Total}^{Alloy} - \left[ 1 - x E_{Solid}^{Ni} + x E_{Solid}^{Cu} \right] \]  

where \( E_{Total}^{Alloy} \) is the total energy of the alloy composition, \( E_{Solid}^{Ni} \) and \( E_{Solid}^{Cu} \) are the total energies of the ground-state structures of elemental Ni and Cu, whereas \( x \) and \( 1-x \) refer to the
fractional concentrations of the constituent elements; the total number of atoms in the structure is represented by \( n \).

### 2.2 Elastic properties

The stress-strain relation may be used to distinguish the elastic and plastic regimes of solid materials. The elastic moduli are the fundamental physical parameters that establish the stress-strain relation in the elastic regime. For an isotropic polycrystalline solid, the two independent elastic parameters are the bulk modulus \((B)\) and the shear modulus \((G)\). The ratio of \(B/G\) predicts the brittleness of metals, depending on the threshold value of 1.75 (ductile if above 1.75) [17]. For the cubic structures, only three elastic constants, corresponding to \(C_{11}, C_{12}\), and \(C_{44}\), are independent. The mechanical stability criteria of cubic crystals are given by the expressions in equation 2.

\[
\begin{align*}
C_{11} > 0, C_{44} > 0, C_{11} - C_{12} > 0, C_{11} + 2C_{12} > 0 \\
B_V = B_R = \frac{1}{3} (C_{11} + 2C_{12}), C' = \frac{C_{11} - C_{12}}{2}, G_H = \frac{G_V - G_R}{2}, E = \frac{9B_H G_H}{3B_H + G_H}
\end{align*}
\]

where \(E\) is the modulus of elasticity, \(G\) trigonal shear modulus, \(B\) bulk modulus, \(C'\) tetragonal shear modulus and anisotropic factor \(A\).

In order to determine the hardness of these systems from first-principles calculations, the empirically model proposed by Chen et al [18], as shown below, is employed as it correlates the elastic moduli \((B\) and \(G\)) with hardness.

\[
H = 2(k^2 G)^{0.585} - 3
\]

where \(k = \frac{G}{B}\) is the Pugh’s modulus ratio.

Chen et al proved that hardness does not only correlates with shear modulus but also with bulk modulus. Now, since the elastic bulk and shear moduli can be accurately calculated by the state-of-the-art first-principles calculations, this model can be used to calculate reliable hardness.

### 3 Results and discussion

#### 3.1 Phase stability

The optimised lattice parameters and the calculated heats of formation of PM and FM FCC Ni-Cu alloy compositions are shown in Figure 2. As observed in Figure 2(a), the lattice
Fig. 2. The lattice parameters and magnetic moment (a) and heats of formation (b) for binary Ni-Cu alloy compositions.

parameter of binary Ni-Cu alloy compositions increases linearly with increase in Cu concentration. This increase is mainly attributed to the fact that the atomic radius of Cu (128 Å) is larger than that of Ni (125 Å). However, this lattice parameter trend is also accompanied by a slight deviation from Vegard’s law. This deviation is more pronounced in alloys at PM state alloy than those in FM state. For Ni-Cu alloys in FM state, increase in Cu composition results in a linear decrease in magnetic moment. An extrapolation from this graph indicates that the material becomes paramagnetic at Cu composition slightly above 30 at.%. The current predicted magnetic trend is in excellent agreement with the Curie temperature ($T_C$) results shown in Figure 1 [8]. From the calculated heats of formation results shown in Figure 2(b), it is clear that $\Delta H>0$ for both systems, although more positive values are obtained in FM state. Although Turchanin et al [8] reported a similar trend commonly associated with miscibility gap, we are of the opinion that to improve the reliability of calculated heat of mixing for solid solution using a supercell approach requires introduction of the entropy term, to result in Gibbs free energy.
3.2 Elastic properties

The calculated elastic properties of the binary PM FCC Ni-Cu alloy compositions are presented in Figures 3. In general, the increase in Cu content results in a gradual decrease in $C_{11}$ and $C_{12}$ elastic constants with a slight increase in $C_{44}$, see Figure 3(a). However, the tetragonal shear $C'$ shows a rather interesting trend with maxima at 12.5 and 22 at.% Cu composition. A similar trend is observed in Figure 3(b) for Young's modulus $E$, predicting maximum alloy stiffness at 22 at.% Cu as opposed to common view of maximum stiffness at 40 at.% Cu. In addition, this increase in $E$ corresponds with a gradual decrease in bulk modulus $B$. Interestingly, amongst the calculated elasticity ratios, the trend of the anisotropic factor $A$ is exactly opposite that of $C'$ and $E$. Furthermore, both ratios show lowest values at 22 at.% Cu, signalling lowest ductility and flexibility for $B/G$ and $A$, respectively. The values of these ratio increase on both sides of the minima. The elastic properties for binary Ni-Cu alloy compositions in FM state are presented in Figure 4. All elastic constants as well as the tetragonal shear $C'$ decrease gradually with Cu addition, as shown in Figure 4(a). A similar trend is observed for $E$ and $B$, as shown in Figure 4(b), signalling softening. This is further evidenced by an increase in $B/G$ and $A$ with increasing Cu composition, suggesting higher ductility and flexibility.

![Fig. 3. The elastic properties of PM binary Ni-Cu alloy compositions.](image)
Lastly, the calculated hardness results are presented in Figure 5. Interestingly, Cu addition has opposite effect on the hardness of binary Ni-Cu alloy compositions. Hardening effect is observed in PM alloy compositions reaching maximum hardness at 22 at.% Cu, followed by softening above this composition. On the other hand, hardness decreases almost linearly with increase in Cu for FM Ni-Cu alloy compositions.
Lastly, the calculated hardness results are presented in Figure 5. Interestingly, Cu addition has opposite effect on the hardness of binary Ni-Cu alloy compositions. Hardening effect is observed in PM alloy compositions reaching maximum hardness at 22 at.% Cu, followed by softening above this composition. On the other hand, hardness decreases almost linearly with increase in Cu for FM Ni-Cu alloy compositions.

4 Conclusion

This first-principles study provided a better understanding of the effect adding Cu to Ni in terms of structural and elastic properties changes. From this study, it is revealed that Cu alloying affects mechanical properties of Ni differently depending on the magnetic state of alloy. In addition, based on this ground-work, key mechanical properties such as $B/G$ and $A$ that are related to wear resistance are identified. In general, the trends of both properties decreased and increased at 22% Cu in PM and FM states, respectively, corresponding to reduced and increased ductility and flexibility. Henceforth, these vital property factors will be useful in screening suitable ternary alloying elements required to overcome unsatisfactory wear performance of Ni-Cu alloys.

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References